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# EVALUATION OF FERRIC CHLORIDE AS A TRACER IN AQUEOUS SPRAYS FOR ASSESSMENT OF FOREST SPRAYING[1]

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## ABSTRACT

*Ferric chloride (0.4%) was an effective tracer for monitoring Thuricide 16B® (64 ounces Thuricide + 16 ounces $H_2O$) spray deposit on both untreated Kromekote® cards and 10% tannic acid-treated Kromekote cards during an operational project. Addition of $FeCl_3$ turned the tank mix black as if a dye had been added. Although a greater number of small drops were detected by the Quantimet on cards previously treated with 10% aqueous tannic acid, recovery rates, expressed in gallons per acre, on both treated and untreated card types did not differ significantly.*

## INTRODUCTION

During the past 25 years, many types of dyes and flourescent tracers have been added to spray mixtures to account for the fate of aerial sprays applied in forests (Neisess 1978). Addition of these materials to pesticide formulations has helped determine quality of application, spray accountancy, and characteristics of spray deposits of various formulations.

Selection of appropriate dyes or tracers should be based upon the following criteria: (1) compatibility with the spray formulation, (2) desired accuracy of spray deposit assessment, (3) ease of handling, and (4) cost and availability.

Quantimet® Image Analzyers can be conveniently used for determining spray deposit on Kromekote cards. Dyes or tracers with sufficient contrast must be used when image analysis to size and count stains is to be performed. Materials used in the past for these purposes, such as Rhodamine B® and Oil-Red® dyes, fade when exposed to sunlight for prolonged periods, thus providing insufficient contrast and poor definition. They also require extra care in handling because spills produce bright red stains which are difficult to remove from aircraft, related equipment, and pesticide loading areas.

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A ferric chloride/tannic acid spray deposit assessment method developed by Maksymiuk (1976) was designed to be used in lieu of the addition of dyes to aqueous sprays for spray deposit assessment. Kromekote cards, dipped in a 10% tannic acid solution react to spray droplets containing $FeCl_3$, producing purple to black stains, dependent upon the concentration of $FeCl_3$.

Tests at the Forestry Sciences Laboratory in Corvallis, Oregon, indicate that a 0.4% weight/volume ferric chloride solution, when applied to 10% tannic acid-treated Kromekote cards, produce stains capable of being readily sized and counted by the Quantimet Image Analyzer. Based on these analyses, it was decided that 0.4% ferric chloride solution be evaluated for operational use. When addition of $FeCl_3$ caused the tank mix to turn black, a secondary objective was developed. Differences between pairs of deposit cards, one treated with a 10% tannic acid solution and one untreated, were to be quantified by the image analyzer.

## MATERIALS AND METHODS

### Project Location

This evaluation was conducted during a 21,000-acre operational spray project using Thuricide 16B (64 oz. Thuricide 16B + 16 oz. $H_2O$) against eastern spruce budworm, Choristoneura fumiferana Clemens. The project, designed and conducted by the Methods Application Group during May 1978 in cooperation with the State of Maine Forest Service and the University of Maine, was located on private land in an area approximately 20 miles northwest of Princeton, Maine.

### Spray Material

A 0.4% $FeCl_3$ solution was prepared by first dissolving 1,965.6 grams of technical grade ferric chloride in lump form ($FeCl_3 \cdot 6\ H_2O$) in one gallon of water. Approximately 15 minutes of stirring was required to dissolve the lumps. This solution was then added to 130 gallons of tank mix containing 104 gallons of Thuricide 16B and 26 gallons $H_2O$. The entire tank mix was prepared, thoroughly agitated, and recirculated for 10 minutes before the day's spray application.

### Placement of Deposit Cards

Twenty pairs of spray deposit cards were placed in the forest approximately 20 feet apart, adjacent to a logging road in one of the spray blocks. Each pair contained an untreated Kromekote card and a tannic acid-treated Kromekote card, prepared according to Maksymiuk (1978). The cards, in plastic holders, were placed on the ground in the morning prior to spraying.

## Aerial Spraying

Approximately 50 gallons of the spray mix was applied per load by a Bell G47 helicopter equipped with four Beecomist Model No. 365 nozzles. Spray was released approximately 50 feet above the canopy at 45 mph indicated air speed.

## Determination of Spread Factor

Spread factors of the mix on untreated Kromekote cards and Kromekote cards treated in a 10% tannic acid solution were determined using methods described by May (1950) and Maksymiuk and Moore (1962).

## Image Analysis

Stains on the spray cards were sized and counted by a Quantimet Image Analyzer equipped with a Plumbicon Scanner and a 63 mm lens, located at the Forestry Sciences Laboratory, Corvallis, Oregon. Number of drops/$cm^2$ and gallons/acre were determined for each card; volume median diameter (VMD), number median diameter (NMD), $\overline{X}$ number of drops/$cm^2$, and $\overline{X}$ quantity of spray deposit expressed in gallons/acre were determined for each of the two sets of spray cards. Two 9.89 $cm^2$ areas were analyzed on each card, and stains were counted and apportioned into 14 size classes.

## Statistical Analysis

A paired t-test (Snedecor and Cochran 1968) was made for each of the two parameters per card, drops/$cm^2$ and gallons/acre. The hypothesis that there are no differences in detection by the image analyzer on the two types of cards was tested at the 95% level and confidence intervals for the mean differences were determined.

# RESULTS

The addition of ferric chloride to the formulation turned the mix black, as if a dye had been added. This reaction was unexpected. Previous testing of $FeCl_3$ with Thuricide 16B in 1975 had not indicated any change in the color of the mix[3]. $FeCl_3$ does react with Shade $^R$, producing a similar black-colored solution[4]. There was no resulting coagulation or precipitation, and no clogging of the spray system or change in rate of flow of the material observed during application.

Spray droplets were recorded on only eight of the 20 pairs of spray deposit cards. No droplets were recorded in the upper six size classes.

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[3] Personal communication with Bohdan Maksymiuk, August 17, 1978.

[4] Personal communication with John Neisess, May 19, 1978.

The results of Quantimet analyses of the pairs, both drops/cm$^2$ and gallons/acre, are given in Tables 1 and 2, respectively. The means, mean differences, and t-values are also shown in these tables.

Table 1. Comparison of number of drops/cm$^2$ on pairs of deposit cards used to sample spray deposit--Northern Maine 1978.

| | Number of Drops/cm$^2$ | | |
|---|---|---|---|
| Pair Number | 10% Tannic Acid Card $X_1$ | Untreated Card $X_2$ | Difference $D = X_1 - X_2$ |
| 1 | 20.4 | 15.3 | 5.1 |
| 2 | 20.3 | 9.8 | 10.5 |
| 3 | 46.6 | 39.5 | 7.1 |
| 4 | 29.4 | 17.4 | 12.0 |
| 5 | 23.4 | 11.6 | 11.8 |
| 6 | 13.6 | 6.6 | 7.0 |
| 7 | 20.1 | 13.5 | 6.6 |
| 8 | 0.7 | 5.9 | -5.2 |
| Mean | 21.8 | 15.0 | 6.86 |

The computed t-value of 3.52 is significant at the .05 level ($t_{.05}$, 7 = 2.365).

Table 2. Comparison of gallons/acre on pairs of deposit cards used to to sample spray deposit--Northern Maine 1978.

| | Gallons/Acre | | |
|---|---|---|---|
| Pair Number | 10% Tannic Acid Card $X_1$ | Untreated Card $X_2$ | Difference $D = X_1 - X_2$ |
| 1 | .08 | .12 | -.04 |
| 2 | .10 | .06 | .04 |
| 3 | .27 | .29 | -.02 |
| 4 | .26 | .16 | .10 |
| 5 | .16 | .06 | .10 |
| 6 | .07 | .06 | .01 |
| 7 | .16 | .13 | .03 |
| 8 | .03 | .08 | -.05 |
| Mean | .14 | .12 | .02 |

The computed t-value of 1.04 is not significant at the .05 level ($t_{.05}$, 7 = 2.365).

At the 95% level, testing differences in numbers of drops/$cm^2$, the hypothesis that there are no differences between the two types of cards is rejected. The Quantimet consistently read a greater number of drops on the tannic acid-treated cards exempting one observation (see Table 3).

There was no statistically significant difference in estimates of gallons/acre for the two types of cards at the 95% level (see Table 2).

A difference in drops/$cm^2$ but not in gallons/acres indicates that smaller stains were detected on tannic acid-treated Kromekote cards. These small drops did not contribute significantly to mass recovery; therefore, significant differences in gallons/acre were not detectable. Both the VMD and NMD were smaller on the tannic acid-treated set of cards than on the untreated set (Table 4). These two measures help to substantiate the conclusion that smaller droplets were found on the tannic acid-treated cards.

Table 4. Overall values for Volume Median Diameter (VMD) and Number Median Diameter (NMD) for each set of cards.

| | Tannic Acid-Treated Card | Untreated Card |
|---|---|---|
| Volume Median Diameter | 165 μm | 173 μm |
| Number Median Diameter | 67 μm | 74 μm |

Spread factors for both types of cards were similar, indicating very little difference, if any, in spreadability of the material on the two types of cards (Figs. 1 and 2).

Tannic acid-treated cards tended to "yellow" after prolonged exposure to sunlight, however, this had no apparent effect upon stain contrast or the ability of the Quantimet to detect stains. Although the cards had been placed on the ground, there was no evidence of accumulated moisture.

## DISCUSSION AND CONCLUSIONS

Ferric chloride as a tracer material is simple to use and goes into solution readily. It is superior to dyes in its relative ease of handling since it does not stain personnel, equipment, or aircraft as do other dyes or tracers. No operational problems, e.g. clogging of Beecomist nozzles, change in rate of flow, etc., were noted with the addition of $FeCl_3$ to the tank mix.

The material proved to be an effective tracer for monitoring spray deposit on either type of card during this operational project. Ferric chloride, in this test, essentially dyed the spray black, negating the

Table 3. Quantimet detection of numbers of stains, by size class, on untreated Kromekote cards and 10% tannic acid-treated Kromekote cards.

| | Size Classes (μm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Card No. | 1 ≤89 | 2 90-178 | 3 179-267 | 4 268-356 | 5 357-445 | 6 446-534 | 7 535-623 | 8 624-712 | 9 713-801 |
| Untreated | | | | | | | | | |
| 1 | 151.5 | 82.5 | 32.5 | 11.5 | 4.0 | 1.5 | 1.0 | 0.5 | |
| 2 | 96.5 | 54.0 | 23.5 | 7.5 | 1.5 | 0.5 | | | |
| 3 | 391.0 | 252.0 | 104.5 | 32.0 | 7.5 | 1.0 | 0.5 | | |
| 4 | 172.0 | 103.5 | 39.5 | 19.0 | 9.0 | 2.0 | 0.5 | 0.5 | |
| 5 | 114.5 | 67.5 | 21.0 | 5.5 | 1.5 | 0.5 | | | |
| 6 | 65.5 | 39.0 | 18.5 | 8.0 | 3.0 | | | | |
| 7 | 134.0 | 85.0 | 14.0 | 6.0 | 2.0 | | | | |
| 8 | 58.0 | 29.5 | 15.0 | 7.5 | 4.5 | 2.0 | 1.5 | | |
| Total No. Drops | 1183.0 | 713.0 | 268.5 | 97.0 | 33.0 | 7.5 | 3.5 | 1.0 | |
| Treated | | | | | | | | | |
| 1 | 202.0 | 105.5 | 32.5 | 7.5 | 2.0 | 1.0 | | | |
| 2 | 200.5 | 124.0 | 40.0 | 12.0 | 2.5 | | | | |
| 3 | 460.5 | 299.0 | 105.5 | 27.0 | 9.0 | 2.5 | 1.0 | | |
| 4 | 291.0 | 194.5 | 82.0 | 20.5 | 11.0 | 4.5 | 2.5 | 1.0 | 0.5 |
| 5 | 232.0 | 154.5 | 59.0 | 16.0 | 6.0 | 1.5 | 0.5 | | |
| 6 | 134.5 | 67.0 | 22.5 | 6.0 | 2.5 | 0.5 | 0.5 | 0.5 | |
| 7 | 198.5 | 126.5 | 57.0 | 20.5 | 5.0 | 2.5 | 0.5 | | |
| 8 | 6.5 | 4.0 | 3.0 | 2.5 | 2.5 | 2.0 | 0.5 | | |
| Total No. Drops | 1725.5 | 1075.0 | 401.5 | 112.0 | 40.5 | 14.5 | 5.5 | 1.5 | 0.5 |

need for a tannic acid-treated deposit card; however, in the absence of the black color, spray droplets containing $FeCl_3$ would not be detected on untreated Kromekote cards. Other aqueous tank mixes may or may not react with $FeCl_3$ in this manner.

Although a greater number of drops were detected by the Quantimet on tannic acid-treated Kromekote cards, the recovery expressed in gallons per acre, was approximately the same.

Because of the time and expense involved in preparation of tannic acid-treated deposit cards, untreated Kromekote cards would adequately monitor this spray formulation on a project of this type. Perhaps use of tannic acid-treated Kromekote cards could be justified if a particular interest in monitoring drift or collection of very fine drops (<50 μm) exists, or if the mix does not turn black.

Ferric chloride as a tracer in other water-base formulations, should be tested for physical, chemical, and biological compatibility prior to use.

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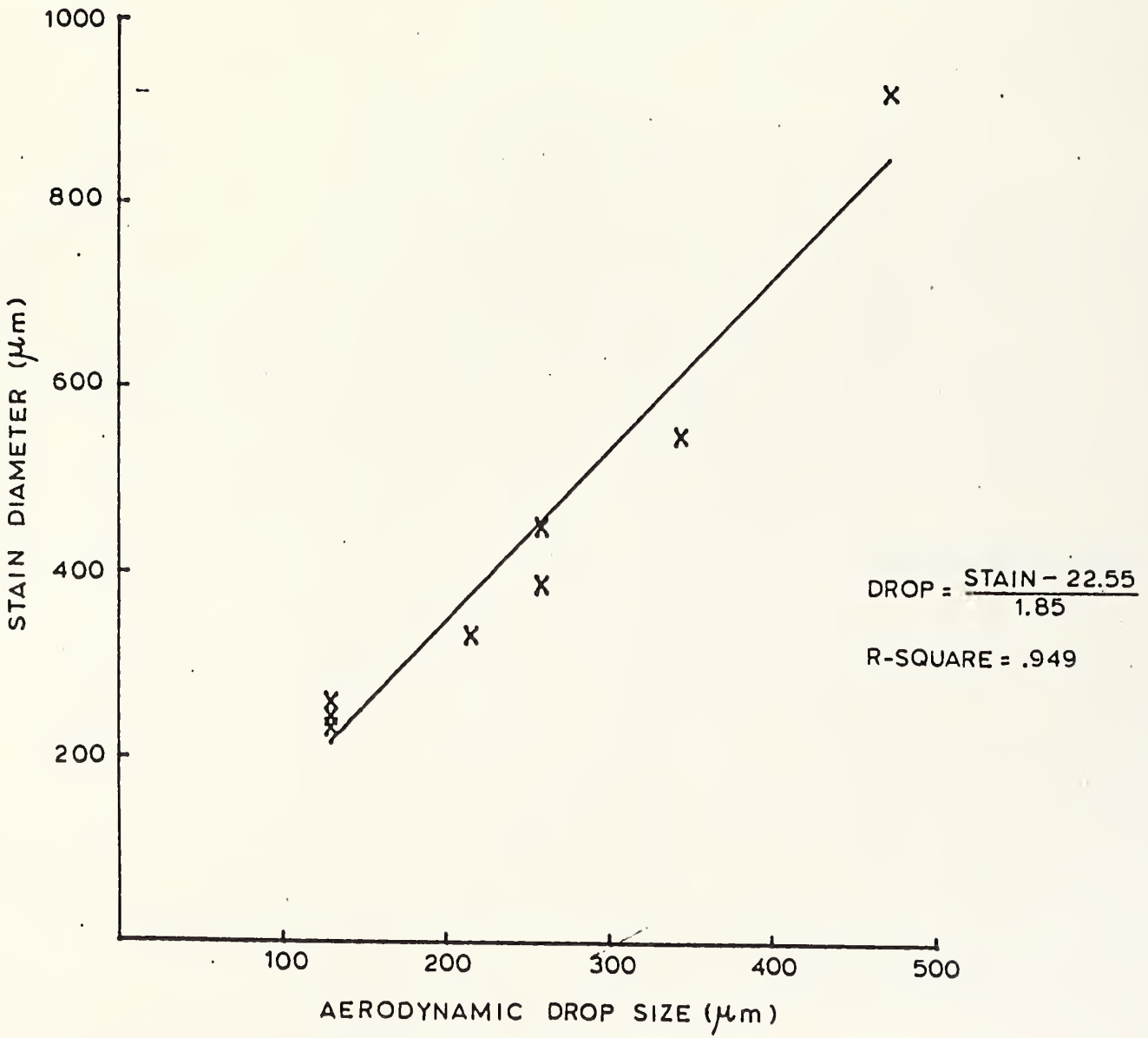


Figure 1. Spread factor of spray formulation (64 oz. Thuricide 16B, 16 oz $H_2O$, 0.4% $FeCl_3$) on untreated Kromekote cards.

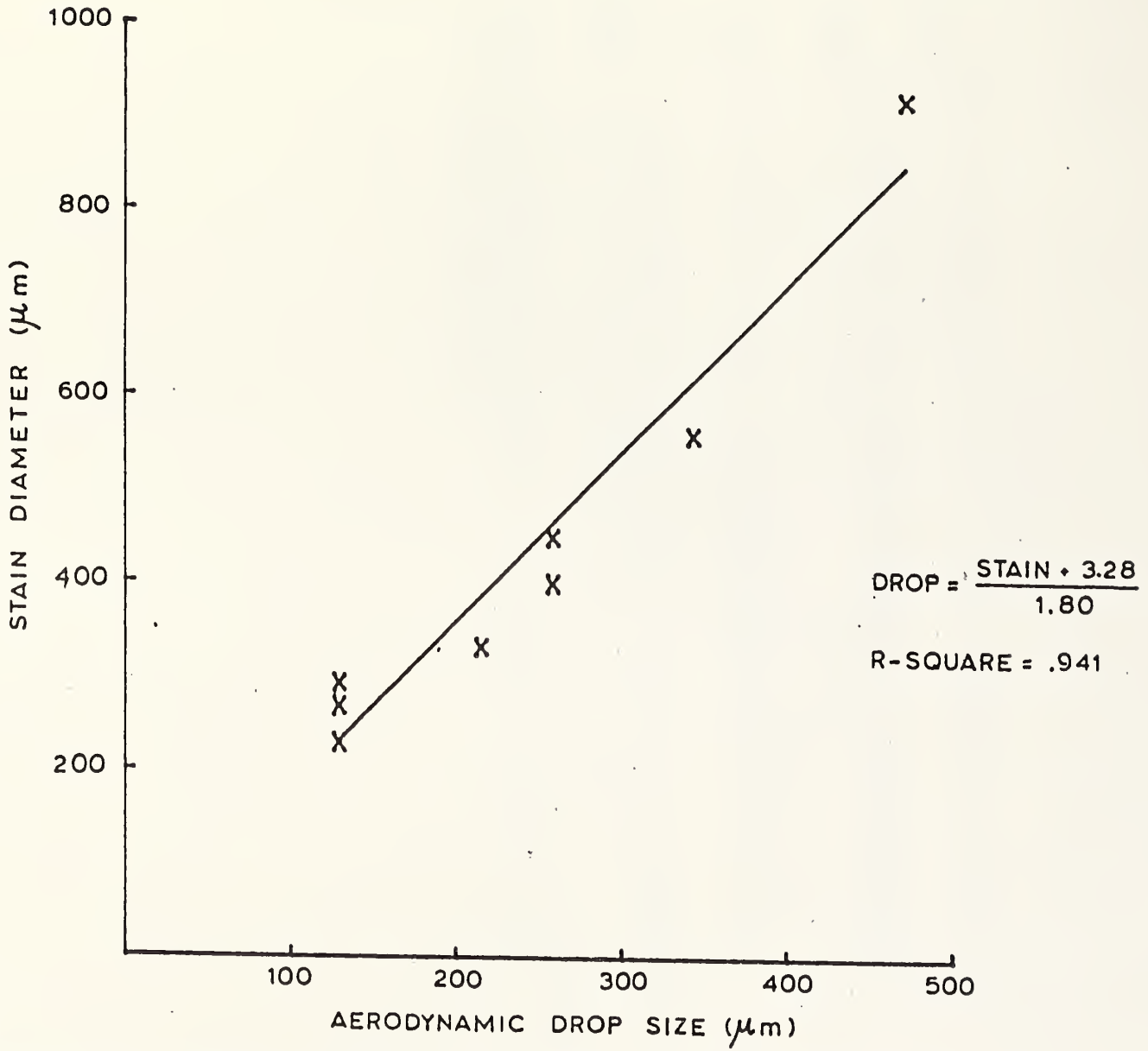


Figure 2. Spread factor of spray formulation (64 oz. Thuricide 16B, 16 oz. $H_2O$, 0.4% $FeCl_3$) on 10% tannic acid-treated Kromekote cards.

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